

# Toluene Oxidation Investigations in a Chamber: TOXIC

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## (1) Introduction

Despite the significance of tropospheric aromatic oxidation to air quality and the associated consequences for human health (both through the highly efficient formation of ozone and secondary organic aerosols (SOA)), the detailed mechanisms, which are crucial components of air quality models, are still poorly understood (Calvert et al. (2002)). The papers by Bloss et al. (Bloss et al. (2006a); (2006b); (2006c)) that resulted from previous EUPHORE experiments (on which MCM<sup>1</sup> version 3.1. is based), show that despite much laboratory work over the past decade, there are still large uncertainties in the mechanisms which culminate in a general over prediction of the peak ozone concentrations, under estimation of the oxidative capacity of the system and under prediction of the NO oxidation rate.

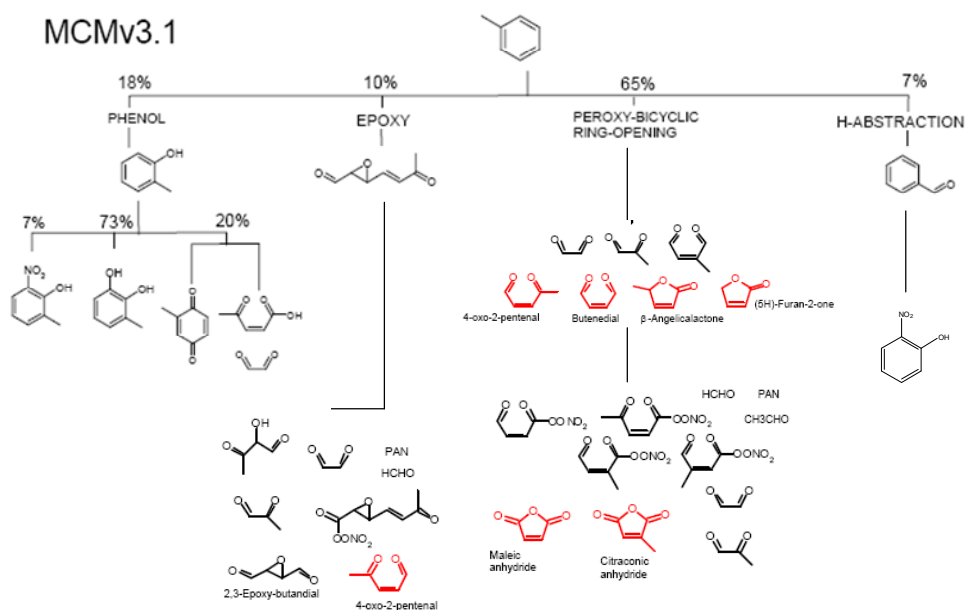
Three key areas where improved information is required have been identified:

- a) **Closure of the primary organic product yields, and improved quantification of channel importance.**
- b) **Improved understanding of the further oxidation of primary oxidation products**
- c) **Secondary radical sources**

One of the main issues in investigating aromatic oxidation is the fact that the time dependent evolution of the intermediate radical and stable products is hard to follow sensitively and accurately (e.g. the O<sub>2</sub>-bridged bicyclic oxygenated and nitrated ring retained products, and the  $\alpha,\beta$ -unsaturated- $\gamma$ -dicarbonyl and  $\alpha$ -dicarbonyl ring opening products (see Figure 1 and Wyche et al. (2009); Rickard et al. (2009)). Information on the further oxidation of primary oxidation products would also be extremely useful in elucidating the radical formation chemistry in the latter stages of oxidation. It has been 5-6 years since the last “Effects of the Oxidation of Aromatic Compounds in the Troposphere” (EXACT) aromatic campaign at EUPHORE and instrumental technology has rapidly moved forward so that we can now sensitively measure the species involved in aromatic oxidation on short temporal scales, information that is needed to develop and evaluate mechanisms such as the MCM. We can also pin down the chamber specific (wall) chemistry in more detail than before owing to the advent of the fast and sensitive LOPAP (Long Path Absorption Photometer) technique for measuring HONO (e.g. see Metzger et al. (2008)).

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<sup>1</sup> <http://mcm.leeds.ac.uk/MCM>



**Figure 1.** Schematic representation of the MCMv3.1 representation of the toluene photo-oxidation mechanism (adapted from Bloss et al. (2005b) and Hamilton et al. (2006))

## (2) Experimental

The EUROCHAMP2 supported TOXIC campaign comprised of a short series of experiments carried out at EUPHORE from the 15<sup>th</sup> to the 31<sup>st</sup> July 2009, primarily focusing on the toluene system. Toluene is of particular importance, owing to its large individual contribution to anthropogenic aromatic hydrocarbon emissions. However, toluene can also be used as a model aromatic system as various aspects of its photochemistry can be extrapolated to other important alkyl aromatic systems and we can use the results to identify the most important steps in aromatic photo-oxidation, where the chemistry is still uncertain. The experiments focused on the photo-oxidation of toluene under different NO<sub>x</sub>/VOC conditions. Some experiments were also carried out on selected toluene oxidation subsystems (i.e. *E*-butenedial, methyl catechols and benzaldehyde). In particular, catechol chemistry is not well defined. Table 1 gives a list of all experiments carried out as part of TOXIC. On some of the days the wind speed was too high to open the chamber, therefore some innovative experiments were performed with the chamber closed. The ozonolysis of tetra methyl ethylene (TME, 2,3-dimethyl-2-butene) was used as an OH source in these experiments.

In addition to the main TOXIC experiments a set of chamber characterisation experiments were carried out directly after the campaign in order to elucidate the chamber auxiliary chemistry. Such experiments are needed to characterise chamber dependent processes, including: the introduction of free radicals from heterogeneous wall reactions, (light dependent) adsorption/desorption of NO<sub>y</sub> species (including HONO) to/from the walls and off-gassing of various reactive species from the walls. In particular, the monitoring of HONO using the LOPAP instrument (see Table 2) is crucial during these experiments (Metzger et al. (2008)). These characterisation experiments included chamber background experiments, ethene (high and low NO<sub>x</sub>, see Zador et al. (2005, 2006)) and HCHO/CO experiments (Zador et al. (2006)).

EUPHORE is highly instrumented with FTIR, DOAS, LIF, LOPAP, GC and HPLC as well as a suite of monitors, radiation and aerosol measurements available. Additional

state of the art instrumentation are required to truly characterize the oxidation processes. The specialist instruments deployed to EUPHORE during TOXIC include the University of Leicester’s Chemical ionization reaction time-of-flight mass spectrometer (CIR-TOF-MS) and the University of York’s high sensitivity NO<sub>x</sub> instrument. York also supplied off-line filter analysis (including time resolved sampling with a Particles-Into-Liquid-Sampler (PILS)) of the aerosols formed using 2D GC and LC-MS-MS techniques in order to look at the detailed composition of the SOA formed (see section (3)).

**Table 1.** The TOXIC Experiments (all concentrations are in ppbV)

DATE	AM	PM	VOC	NO	TME	O <sub>3</sub>	VOC/NO <sub>x</sub>
15-July	SET UP/CAL	SET UP/CAL	—	—	—	—	—
16-July	SET UP/CAL	SET UP/CAL	—	—	—	—	—
17-July	SET UP/CAL	SET UP/CAL	—	—	—	—	—
20-July	TOLUENE	LOW NO <sub>x</sub>	535	59.9	—	—	8.93
21-July	TOLUENE	MOD NO <sub>x</sub>	558	148.2	—	—	3.77
22-July	TOLUENE	LOW NO <sub>x</sub>	501	53.5	—	—	9.36
23-July	TOLUENE	DARK	800	—	300	200	—
24-July	TOLUENE	HIGH NO <sub>x</sub>	381	350.4	—	—	—
27-July	<i>E</i> -butenedial (zero NO <sub>x</sub> )	<i>E</i> -butenedial (NO <sub>x</sub> )	225 (am) 130 (pm)	— 530	— —	— —	— 0.25
28-July	4-methyl catechol (DARK)	4-methyl catechol (PHOTO)	500 (am) 500 (pm)	— 150	300 —	200 —	— 3.33
29-July	Benzaldehyde	MOD NO <sub>x</sub>	500	145.2	—	—	3.44
30-July	TOLUENE	MOD NO <sub>x</sub>	488	147.0	—	—	3.32
31-July	CAL/BLANK	TAKE DOWN	—	—	—	—	—

Toluene forms glyoxal and methyl glyoxal as primary ring opening products (see Figure 1). In order to measure the evolution of these species sensitively and accurately Leicester’s Broadband Cavity Enhanced Absorption Spectrometer (BCEAS) was run in concert with DOAS, CIR-TOF-MS and Solid Phase Micro Extraction (SPME) techniques during TOXIC. The abundance of instruments that can sensitively measure glyoxal and methyl glyoxal is extremely useful for looking in detail at the primary and secondary yields of  $\alpha$ -dicarbonyls, and hence the primary and secondary chemistry of toluene photo-oxidation. Also, there is obviously considerable scope for intercomparison. In order to calibrate the SPME instrument and to provide reagents for the experiments, the organic synthesis group of Professor Bernard Golding at the University of Newcastle was employed to synthesise the ring opening products *E* and *Z*-butendial, 2-methyl butendial and 4-oxo-2-pentenal. The

National Centre for Atmospheric Science (NCAS) provided significant logistical support for the transportation of these instrumentation to/from EUPHORE. Table 2 gives a list of instrumentation used /measurements taken during the TOXIC experiments.

The mechanistic insights gained from this short, focused series of experiments will be used to evaluate and inform development of, and refine the aromatic chemistry in, the Master Chemical Mechanism.

**Table 2.** Summary of the available instrumentation

INSTRUMENT	COMMENT	TARGET SPECIES/COMMENTS <sup>a</sup>
LIF	FAGE <sup>b</sup> (CEAM)	OH, HO <sub>2</sub> (0.1/0.24 pptv; 1 min)
CIR-TOF-MS	University of Leicester (Monks/Ellis/Wyche)	VOCs and OVOCs (sub ppbv and possibly pptv; 1-10 min) Glyoxal (HCOHCO) (120ppb, 10 min) Methyl glyoxal (CH <sub>3</sub> COCO) (15-60ppb, 1 min / 1-10ppb, 10 min) Formaldehyde (HCHO) (15 ppbv, g, 1 min) Acetaldehyde (HCHO) (5 ppbv, 1 min) Formic Acid (HCOOH) (15 ppbv, 1 min) Acetic Acid (CH <sub>3</sub> COOH) (8 ppbv, 1 min)
BBCEAS <sup>b</sup>	University of Leicester (Ball)	Glyoxal (sub ppbv; 1 min) Methyl glyoxal (sub ppbv; 1 min) NO <sub>2</sub> (sub ppbv; 1 min)
GC-FID	Hewlett-Packard 6890 (CEAM)	VOC and OVOC (sub ppbv, 10 min)
HPLC – UV/FLD	CEAM	VOCs and OVOCs (e.g. phenol, cresols, catechols); sub ppbv Hydroperoxides
FTIR	Magna 550, 654 m path (in-situ white cell) (CEAM)	O <sub>3</sub> , VOCs and OVOCs (1 cm <sup>-1</sup> resolution, few ppbv; 10-15 min integration time)
DOAS	CEAM	NO <sub>2</sub> , HCHO, OVOCs, ( <i>ca.</i> 1 ppbv; 10 min integration) Glyoxal, (0.5 ppbv; 10 min) Methyl glyoxal (0.5 ppbv; 10 min)
Ozone monitor	UV Abs, ML 9810 (CEAM)	O <sub>3</sub> (0.65 ppbv; 1 min)
CO monitor	IR absorption, TE48C (CEAM)	CO (5 ppbv; 1 min)
NO <sub>x</sub> Monitor	ECO-Physics CLD 770 AL with photolytic converter (CEAM)	NO <sub>x</sub> (NO+NO <sub>2</sub> ) (0.26 ppbv; 1 min)
NO <sub>y</sub> Monitor	LABS Chemiluminescence with catalytic converter (CEAM)	NO <sub>y</sub> (HONO+NO+NO <sub>2</sub> +PAN+2N <sub>2</sub> O <sub>5</sub> +HNO <sub>3</sub> ) (4.22ppbv; 1 min)
NO <sub>xy</sub> (sensitive)	University of York (NCAS)	Speciated NO <sub>x</sub> (sub pptv; 1 min) ~ 50 pptv for 1 s data or ~5 pptv average up to 1 min.
HONO Monitor	LOPAP <sup>®</sup> Long Path Absorption Photometer (CEAM)	HONO (0.012 ppbv; 30 s)
HCHO analyzer	Aero Laser AL4021	HCHO (0.3 ppb; 15 s)
SPME <sup>b</sup> (GC-MS)	In fibre reaction with PFBHA <sup>b</sup> (CEAM)	Glyoxal (0.1-0.5ppbv; 5-10 min) Methyl glyoxal (0.5 ppbv; 5-10 min)
PAN GC	PAN GC Schmitt/Glasheutten (CEAM)	Peroxy Acetyl Nitrate (0.15 ppbv; 10 min) Methyl glyoxal (0.5 ppbv; 10 min)
TEOM series 1400a	CEAM	Aerosol Mass Concentration, 1 µm cut off (1 µg m <sup>-3</sup> ; 1 min)

SPMS	3080 TSI (CEAM)	particle number and aerosol volume concentrations, D = 10-1000 nm
Filters - GC-MS	HP GC5890 MS 5989 series II (CEAM)	SOA compounds: semi-quantitative speciation of acids, carbonyls, hydroxyl carbonyls (1-5 ng; 1 h), off line analysis
Filters (GC×GC/LC-MS-MS/GC×GC-NCD)	University of York (Hamilton)	SOA composition (off line analysis)
PILs Sampling	University of York (Hamilton)	Particles Into Liquid sampling – time resolved aerosol sampling, off line analysis of water soluble organic aerosol
Diode array spectroradiometer ( <i>j</i> -values)	CEAM (Chamber B) University of Leicester (Monks)	Actinic Flux (2π and 4π sr); high resolution measurement of large range of photolysis frequencies (1 s (averaged to 1 min))
<i>j</i> (NO <sub>2</sub> )	Filter radiometer (CEAM)	4π sr measurement of <i>j</i> (NO <sub>2</sub> ) (1 min)

<sup>a</sup> Detection limit; time resolution; <sup>b</sup> FAGE = Fluorescence Assay by Gas Expansion; BBCEAS = Broad Band Cavity Enhanced Absorption System; GC-MS = Gas Chromatography-Mass Spectrometry; SPME = Solid Phase Micro Extraction; PFBHA= *o*-(2,3,4,5,6)pentafluorobenzylhydroxylamine hydrochloride.

### (3) Future work and some results

The majority of the data analysis/work up has now been carried out and datasets placed on dedicated TOXIC ftp sites in Leeds and EUPHORE. We are now at the stage where we can start to use the data to look at the mechanism(s) in detail. Once we have looked at some preliminary model runs a meeting will be organised in Leeds to discuss further analysis, intercomparisons and projected publications (early Summer 2010).

We will also model the evolution of the toluene gas and aerosol phase composition using a coupled kinetic and aerosol partitioning model, incorporating the MCMv3.1 mechanism for toluene, in order to simulate the mass distributions in the TOF-MS and ESI-MS spectra, in collaboration with the Universities of Birmingham and Manchester (e.g. see Camredon et al. (2009)).

#### (3.1) SOA characterisation

##### (3.1.1) Sampling and Analysis

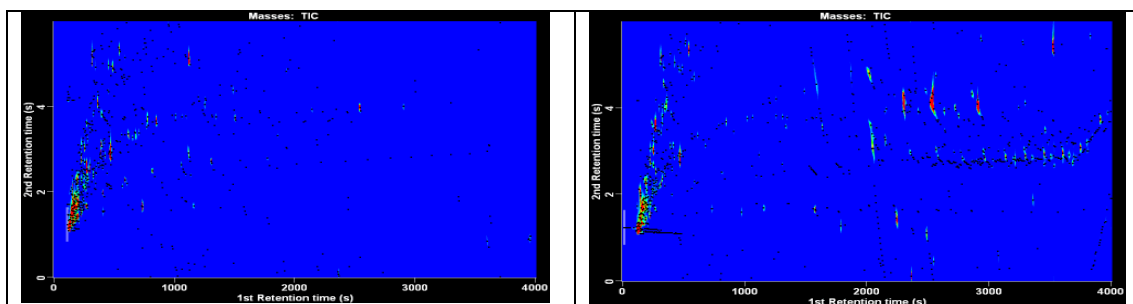
A total of 9 filters were collected during TOXIC for *off-line* analysis at the University of York. Samples were frozen immediately after collection and shipped to York under dry ice to ensure sample integrity. The filters were extracted using two methods:

1. Approximately 80 % of the filter was extracted into methanol for two hours. The extracts were then evaporated to dryness and re-dissolved in 1 ml of methanol. Liquid extracts were analysed using two techniques. Liquid chromatography coupled to ion trap mass spectrometry LC-MS<sup>n</sup> (polar molecules and oligomers) (Hamilton et al. (2008)) and comprehensive two dimensional gas chromatography coupled to a nitrogen specific detector (GCXGC-NCD). This novel instrument gives a response for organic nitrogen species only and has previously not been used for aerosol characterisation work.
2. The remainder of the filters were analysed using direct thermal desorption (DTD) coupled to comprehensive two dimensional gas chromatography with time of flight mass spectrometric detection (Hamilton et al. (2005))

### (3.1.2) Results - SOA composition

All filter samples have been analysed using the three techniques (LC-MS<sup>n</sup>, and GCXGC-NCD). Data analysis is ongoing and preliminary data are shown here.

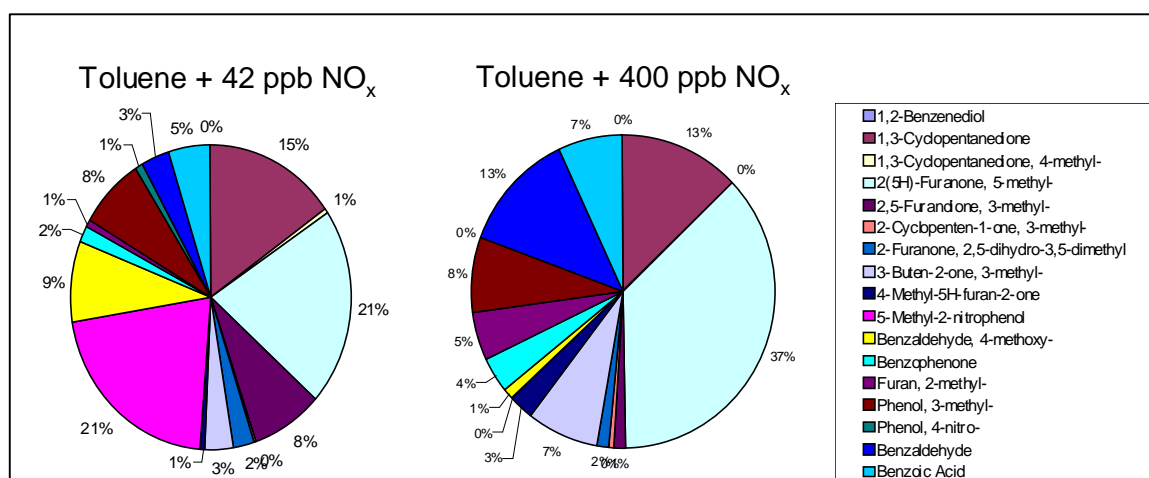
GCXGC-TOF-MS chromatograms are presented as contour plots where the retention times on columns 1 and 2 are given on the X and Y axes respectively, with abundance shown as a coloured contour. Each spot represents an individual compound which has an associated mass spectrum for identification. Example chromatograms are shown in Figure 2 for toluene with low (22/07/09) and high (24/07/09) NO<sub>x</sub> levels. It is clear that the composition of the SOA is different depending on the VOC/NO<sub>x</sub> ratio.



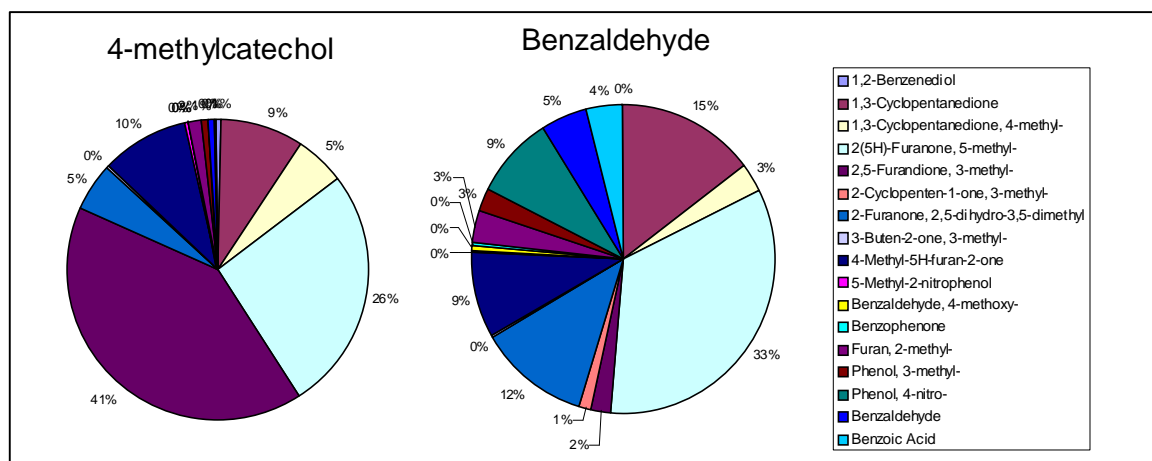
**Figure 2:** GCXGC chromatograms for two experiments. Left: (22/07/09) Toluene (503 ppbV) + NO (~42 ppbV). Right: (24/07/09) Toluene (381 ppbV) + NO (~400 ppbV).

Over 30 compounds have been identified in all TOXIC samples. In order to obtain quantifications, standard mixtures were spiked onto filter papers and analysed using DTD in the same manner as the SOA filters. However, this resulted in very poor reproducibility and could not be used for calibration. Work is ongoing to determine concentrations using liquid extracts. For a preliminary analysis, the areas have been used (since the sensitivity of the instrument for a single compound is consistent between runs) to compare the SOA composition between different samples and oxidation conditions. The pie charts in Figures 3 and 4 show the SOA composition distribution based on 17 compounds only (confirmed structures).

Some of the compounds are difficult to explain mechanistically (such as 1,2,cyclopentanedione) but appear to match well with the NIST Mass Spectral Patterns. Standard mixes will be used to confirm identifications.

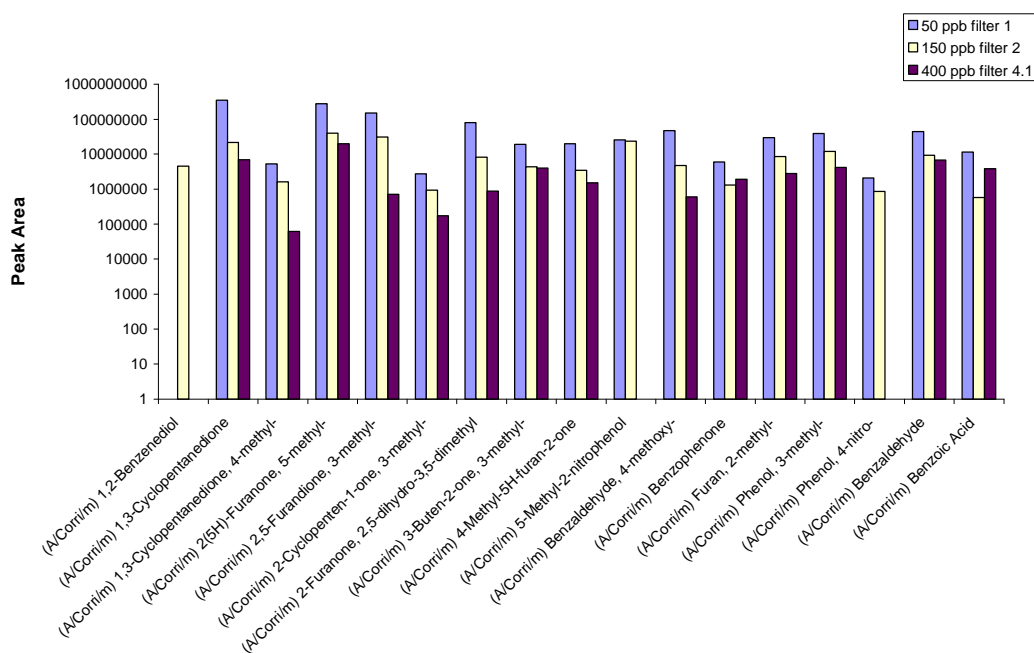


**Figure 3:** SOA distribution of 17 compounds in the TOXIC toluene experiments 22/07/09 (low NO<sub>x</sub>) and 24/07/09 (high NO<sub>x</sub>)



**Figure 4:** Comparison of the SOA distribution of 17 compounds from 4-methyl catechol reactions with OH (28/07/09-pm) and benzaldehyde + OH (29/07/09).

The peak area of each of the 17 compounds in toluene SOA under the three different VOC/NO<sub>x</sub> experimental conditions are shown in Figure 5. The area is plotted on a logarithmic scale to account for the large differences in concentration between samples. The peak areas have been corrected for DTD sample size but not the amount of aerosol collected (i.e. should give a direct comparison of concentrations of an individual compound (ng m<sup>-3</sup>) in each experiment). It is clear that for nearly all compounds the highest concentrations are found in the experiments with the highest VOC/NO<sub>x</sub> ratio. This is also true for the nitro-aromatics species measured using the NCD.



**Figure 5:** Comparison of peak area for 17 compounds found in toluene SOA under three separate VOC:NO<sub>x</sub> conditions.

## (4) References

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